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(54) Anodising Aluminium Substrate for Magnetic Recording Media

(57) An aluminum substrate suitable for making high-density magnetic recording media is produced by anodising a surface of the aluminum material in an aqueous chromic acid solution at an electrolytic voltage higher than 60 volts. The anodic film thus formed has not black spot defects as also exhibits no cracks when the substrate is heated at a high temperature for forming a magnetic recording layer.

The effect is further improved by adding a small amount of oxalic acid to the electrolyte.

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SPECIFICATION

Process of Producing Aluminum Substrate for Magnetic Recording Media

Background of the Invention

Field of the Invention

This invention relates to a process of producing an aluminum substrate for making magnetic recording media, said substrate having an anodically oxidized film or layer on the surface thereof. More particularly, the invention relates to a process of producing an aluminum substrate for making high-density magnetic recording media, said substrate having substantially no black spot defect and having excellent smoothness and heat resistance.

Description of the Prior Arts

Recently, there has been much demands to increase recording density of magnetic recording media, such as magnetic disk, etc. For responding to such demands, it is necessary to reduce thickness of the magnetic medium layer to be formed on a surface of the substrate and the spacing between the magnetic head and the magnetic medium. The substrate of such magnetic recording media is required to have more excellent surface properties with respect to smoothness, and hardness.

As a substrate for making high-density magnetic recording media as above-mentioned, an aluminum substrate having an anodic oxide film on the surface thereof has been used.

Aluminum substrate having such an anodic oxide film is desirable because the anodic oxide film formed on the surface of aluminum is hard and excellent in wear resistance, has good polishability, whereby a smooth surface in high accuracy can be easily obtained, and a thin magnetic layer can easily formed on the surface of it.

Hitherto, for easily forming an anodic oxide film having suitable hardness for making magnetic recording media on an aluminum substrate, commonly an electrolytic treatment using a sulfuric acid solution has been performed as disclosed in the British Patent No. 1,493,160 of Nov. 23, 1977. However, the aluminum substrate having formed thereon an anodic oxide film using a sulfuric acid solution (hereinafter, is referred to as a sulfuric acid anodic oxide film) has the faults as described hereinafter and these faults are obstructs for increasing the recording density of a magnetic recording media.

One of these faults is a so-called black spot defect. Impurities such as iron, silicon, etc., existing in aluminum or an aluminum alloy crystallize as intermetallic compounds, which exist at the surface of aluminum or the aluminum alloy as microscopic spots. Such microscopic spots do not form anodic film properly during electrolytic treatment. The spots are, at the beginning, very fine ones of sub-micron order but become larger with the growth of the anodic oxide film and show pit-like fine defects of 5 to 10 μm in diameter on the sulfuric acid anodic oxide film having a thickness of thicker than 5 μm or more. If an substrate has many of these defects, the signal error in the magnetic recording medium is larger and hence the existence of the defect is undesirable.

Another one of the faults is thermal cracking. In the case of the aluminum substrate for high-density magnetic recording medium, it is required to apply α-Fe_2O_3 to the surface of the aluminum substrate by sputtering or vapor deposition, followed by heating to 300—400°C for forming γ-Fe_2O_3 but when the aluminum substrate is heated to such a high temperature, the sulfuric acid anodic film formed on the substrate is cracked, whereby inferior products are liable to occur. Accordingly, the thickness of the anodic oxide film must be reduced to the extent as thin as 1 to 3 μm, which results in reducing the head crash resistance of the aluminium substrate and hence the occurrence of cracking is undesirable.

As the result of investigation on improving the aluminum substrate having anodic oxide film, the inventors have discovered that when an aqueous chromic acid solution is used for the formation of the anodic oxide film on an aluminum and an electrolysis is performed at a constant voltage method higher than a voltage employed for conventional chromic acid electrolysis, an aluminum substrate having no black spot defects and no thermal cracking can be produced.

Also, it has been discovered that when in the case of forming the anodic oxide film over 10 μm in thickness on an aluminum using the foregoing chromic acid process, a hardness of thus formed film becomes about or over 300 Hv in Vickers hardness, which is required for head crush resistance and scratch resistance in this kind of aluminum substrate.

Summary of the Invention

A primary object of this invention is to provide a process of producing an aluminum substrate for magnetic recording medium having formed thereon an anodic oxide film which is hard, is excellent in heat resistance, and has practically no black spot defects.

Other object of this invention is to provide an aluminum substrate for a high-density magnetic recording medium.

Other objects and effects of this invention will become apparent from the following detailed explanation.

That is, according to this invention, there is provided a process of producing an aluminum substrate for magnetic recording medium which comprises electrolytically treating an aluminum material using a solution containing 1.5 to 15% by weight chromic acid as the electrolyte by a constant voltage higher than 60 volts.

Detailed Description of the Invention

An aluminum material used for the substrate in this invention is high-purity aluminum such as aluminum having a purity of higher than 99.9% or an alloy composed of the foregoing high-purity aluminum as a base metal containing 2 to 6% by weight magnesium. When a high-purity aluminum is used as the aluminum material, the aluminum may be lined with an aluminum alloy or a rigid non-magnetic material such as a hard resin for imparting a strength to the substrate.

Such an aluminum material is formed into a circle or other any desired form and after smoothening the surface thereof by grinding or polishing, an anodic oxidizing treatment is applied onto the surface of the aluminum material using a chromic acid-containing electrolyte.

In this invention, the concentration of an aqueous chromic acid solution used as the electrolyte is 1.5 to 15% preferably 2—5%, the temperature of the electrolyte is 30 to 50°C preferably 33 to 42°C, and the current density is 0.1 to 0.8 amp./dm^2 preferably 0.25—0.65 amp./dm^2, that is, these conditions in this invention are almost same as the conditions in a conventional constant voltage chromic acid anodic oxidizing treatment called "Buzzard process". However, the electrolytic voltage in this invention is higher than the electrolytic voltage, 40 volts in the Buzzard process and is higher than 60 volts, preferably 75 to 100 volts.

In addition, by adding oxalic acid to the electrolyte in an amount not over 1/5 of the amount of chromic acid in the electrolyte, the current density is increased and the film-forming speed and/or the hardness of film can be increased without reducing other effects of this invention. If the concentration of oxalic acid in the electrolyte is over 1/5 of the amount of chromic acid, the thermal cracking resistance of the film formed is reduced and the black spot defect is liable to occur.

Also, if the amount of the aluminum ion existing in the electrolyte increases over a certain limit during the electrolysis of this invention, the current density suddenly decreases to reduce the heat resistance and the hardness of the film formed on the aluminum material. Accordingly, it is desirable to keep the concentration of aluminum ions in the electrolyte below 1/20 of that of chromic acid during the electrolysis.

The aluminum substrate thus obtained has such excellent features suitable for high recording density magnetic recording media that there is practically no formation of fine black spot defects in the aluminum substrate, when the thickness of the film is over 10 μm, the hardness of the aluminum substrate is as good as or higher than that of the aluminum substrate treated by a conventional sulfuric acid process anodic oxidation, whereby the aluminum substrate in this invention is excellent in polishability and scratch resistance, and when the aluminum plate treated in this invention is maintained at 300 to 400°C for forming a magnetic layer on the surface thereof, fine cracks do not develop owing to the excellent heat resistance of the aluminum substrate.

Then, the inventors' experiments performed for completing this invention will be subscribed hereinafter.

Aluminum-magnesium alloy sheets (Al—3% Mg) prepared using high-purity aluminum of 99.99% were subjected to an electrolytic treatment in an aqueous 5% chromic acid solution maintained at 35°C by constant D.C. voltage process and the black spot formation on the treated aluminum substrates at each electrolytic voltage was checked, the result being shown in Table 1. Also, the same specimens were heated to 350°C for 2 hours, and the formation of fine cracks were examined and the result is shown in Table 1 together with the hardness of the film formed on the sheets in connection with the scratch resistance and the headcrash resistance.

Also, for the sake of comparison, the same evaluation tests as above were applied to an aluminum alloy having the same composition, as used in the foregoing tests subjected to conventional sulfuric acid anodic oxidation process (15% H_2SO_4 solution, bath temperature of 20°C, constant voltage process at 10 volts) and the evaluation results are also shown in the same table.

In these tests, the anodic film thickness of the specimens prepared by this invention was 12 μm and that of the specimens by the conventional process was 6 μm.

In the evaluation of the black spot shown in Table 1, O signifies that no or one black spot smaller than 2.5 μm is observed in the microscopic range of field (0.36 mm^2), and Δ signifies no or one black spot smaller than 3.5 μm in the range above mentioned, while X means emergency of more or larger black spots.

Also, the evaluation of the formation of fine cracks was made by microscopic observation of the surface of the aluminum substrate after the application of the foregoing heat treatment. In the evaluation shown in Table 1, O, Δ and X signify no cracking, partial cracking and overall cracking respectively.

The evaluation of the hardness was made using a micro Vickers hardness tester (load 15 g).

TABLE 1

Voltage (Volt)	Black Spot	Crack	Hardness Hv
40	Δ	X	183
60	Δ	Δ	252
80	0	0	313
100	0	0	260
120	Δ	0	225
Conventional process	X	X	290

Also, aluminum alloy specimens each having the same composition as the aluminum alloy used in the foregoing tests were subjected to an anodical oxidation treatment using an aqueous chromic acid solution having the same temperature and concentration as those in the foregoing tests at constant D.C. voltage process of 75 volts to form anodic oxidized films having different thicknesses, respectively and the formation of black spot was examined, the results being shown in Table 2.

Then, the aluminum alloy specimens were maintained at 300°C, 350°C, or 400°C for 2 hours and the cracks were examined in each case. The results are also shown in Table 2.

The evaluation modes of the black spot and the hardness are same as in the foregoing tests shown in Table 1.

TABLE 2

Film Thickness (μm)	Crack			Black Spot	Hardness Hv
	300°C	350°C	400°C		
3	0	0	0	0	165
6	0	0	0	0	245
10	0	0	0	0	298
13	0	0	0	0	325
15	0	0	0	0	315
18	0	0	Δ	0	302
20	Δ	Δ	X	—	285

From the results shown in Figure 1 and Figure 2, the following will be recognized.

That is, in the aluminum substrates treated by the process of this invention, i.e., subjected to the electrolytic treatment using an aqueous chromic acid solution by the constant D.C. voltage process at an electrolytic voltage higher than 60 volts, no or almost no black spot is observed, cracks are not formed by heating for forming a magnetic layer when the thickness of the film is less than about 18 μm, and the aluminum substrate satisfies the hardness required for a substrate of this kind when the film thickness is more than 10 μm. On the other hand, in the aluminum substrate subjected to the electrolytic treatment using an aqueous sulfuric acid solution by a conventional typical anodic oxidation treatment or the aluminum substrate subjected to the electrolytic treatment using an aqueous chromic acid solution under conventional conditions, i.e., at a voltage about 40 volts, it is difficult to satisfy the three criteria for black spot, crack, and hardness.

Then, an aluminum-magnesium alloy substrate having the same composition as that used in the foregoing tests was subjected to an electrolytic treatment in each of electrolytic baths of an aqueous 5% chromic acid solution containing a different amount of oxalic acid at a constant voltage of 90 volts

while varying the bath temperature, and the current density (amp./dm²) and the Vickers hardness Hv (load: 20 g) were measured in each case. The results thus obtained are shown in Table 3. In addition, the thickness of the film formed on the aluminum plate was 13 μm in each case.

TABLE 3

Content of Oxalic Acid (%)	Bath Temperature (°C)					
	30		35		40	
	C.D.*	Hardness	C.D.	Hardness	C.D.	Hardness
0	0.25	280	0.43	339	0.60	278
0.1	0.28	296	0.44	350	0.62	298
0.5	0.29	300	0.46	356	0.64	321

(*): C.D.: Current density

As shown in the results of the above table, it is understood that in the case of using an aqueous chromic acid solution alone, the film formed on the aluminum tends to be softened when the bath temperature is increased but the hardness of the film can be increased even at a high temperature by adding a small amount of oxalic acid to the electrolyte and in the case of using an aqueous chromic acid solution containing an oxalic acid, a film having almost the same hardness as in the case of forming a film by using a chromic acid solution can be obtained at a higher bath temperature than that in the foregoing electrolytic treatment, whereby the current density can be increased and the treatment time can be shortened.

As described above, by the process of this invention, the worst problems in the aluminum substrate for magnetic recording medium, i.e., the formation of black spots, the formation of cracks at high-temperature treatment, and reduction in headcrash resistance and scratch resistance can be solved altogether.

Then, the process of this invention will be further described practically by the following examples.

EXAMPLE 1

After subjecting a disk (inside diameter of 75 mm, outside diameter of 200 mm, and thickness of 2 mm) of an aluminum alloy (Al—3% Mg) prepared using aluminum of 99.99% in purity to an appropriate surface polishing, the disk was rinsed in a non-etching degreasing agent and then subjected to an anodic oxidation treatment. That is, the foregoing aluminum alloy disk was immersed in an aqueous 3.5% chromic acid solution maintained at 35°C and the electrolytic treatment was performed by passing direct current using the aluminum alloy disk as the anode at a constant voltage of 80 volts. By performing the electrolysis for about 60 minutes at a current density of 0.45 amp./dm², an aluminum substrate having an opaque and smooth anodic film of 12 μm in thickness was obtained.

Through the performance of electrolysis a concentration of aluminum ion was kept under 2 g/l.

Then, the disk substrate was polished with a grind medium consisting of fine alumina powder (—3 μm).

The surface roughness of polished substrate was 0.02 μm (Rmax.)

After polishing the disk substrate, the hardness thereof was measured by means of a micro-Vickers hardness tester (load: 15 g). The hardness was 308 Hv.

When the surface of the disk substrate was examined with a microscope, no black spot defect was observed.

Also, when the substrate was further heated to 350°C for 2 hours, no crack was observed on the surface.

EXAMPLE 2

After subjecting a disk substrate (inside diameter pf 75 mm, outside diameter of 200 mm, and thickness of 2 mm) of an aluminum alloy (Al—4% Mg) prepared using aluminum of 99.99% in purity to an appropriate surface polishing, the aluminum disk substrate was immersed in an aqueous 5% chromic acid solution of 35°C containing 1% oxalic acid and the electrolytic treatment was performed at a constant D.C. voltage of 100 volts using the disk as the anode to form an opaque and smooth anodic film of 12 μm in thickness. The current density in the electrolytic treatment was 0.45 amp./dm²

and the treatment time was 45 minutes. Through the performance of electrolysis a concentration of aluminum ion was kept under 2 g/l.

The Vickers hardness (load: 15 g) of the obtained disk substrate after polishing was 351 Hv and when the surface of the disck substrate was examined with a microscope, no black spot defect was observed. Also, when the substrate was further heated to 350°C for 2 hours, no crack was observed on the surface.

CLAIMS

1. A process of producing an aluminum substrate for magnetic recording media, which comprises subjecting an aluminum material to an electrolytic treatment by a constant voltage process at an electrolytic voltage higher than 60 volts using an aqueous solution of 1.5 to 15% by weight chromic acid as the electrolyte.

2. The process of producing an aluminum substrate for magnetic recording media as claimed in claim 1, wherein the electrolytic treatment is performed by a constant voltage process at a voltage of 70 volts to 100 volts.

3. The process of producing an aluminum substrate for magnetic recording media as claimed in claim 1, wherein the aluminum material is high-purity aluminum having purity of higher than 99.9% or an aluminum alloy composed of the foregoing high-purity aluminum as the base metal and 2 to 6% by weight magnesium.

4. The process of producing an aluminum substrate for magnetic recording media as claimed in claim 1, wherein the electrolyte further contains oxalic acid in an amount not over 1/5 of the concentration of chromic acid in the electrolyte.

5. The process of producing an aluminum substrate for magnetic recording media as claimed in claim 1, wherein the electrolytic treatment is performed while keeping the concentration of the aluminum ions in the electrolyte below 1/20 of that of chromic acid.

6. The process of producing an aluminum substrate for magnetic recording media as claimed in claim 1, wherein the thickness of anodic oxide film formed by the electrolysis is from 10 μm to 18 μm.

7. An aluminum substrate for magnetic recording media, which is produced by a process comprising subjecting an aluminum material to an electrolytic treatment by a constant voltage process at an electrolytic voltage higher than 60 volts using an aqueous solution of 1.5 to 15% by weight chromic acid as the electrolyte.

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